

## Structural Analysis and Magnetic Properties of the 1D and 3D Compounds

 $[M_n(\text{dca})_{2n}\text{bipym}]$  ( $M = \text{Mn, Cu}$ ;  $\text{dca} = \text{Dicyanamide}$ ;  $\text{bipym} = \text{Bipyrimidine}$ ;  $n = 1, 2$ )

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Compounds  $[\text{Mn}(\text{dca})_2\text{bipym}]$  (**1**),  $[\text{Cu}_2(\text{dca})_4\text{bipym}]$  (**2**), and  $[\text{Mn}_2(\text{dca})_4\text{bipym}]$  (**3**) have been synthesized and structural (**2**, **3**) and magnetically characterized. Compound **1** is isomorphous with  $[\text{Mn}(\text{dca})_2\text{bipy}]$ . Compound **2** crystallizes in the monoclinic  $P2_1/c$  space group,  $Z = 4$ , with  $a = 7.5609(9)$ ,  $b = 11.477(42)$ , and  $c = 11.792(2)$  Å and  $\beta = 106.565(6)^\circ$ . Compound **3** crystallizes in the monoclinic system, space group  $P2_1/n$ , with  $a = 7.396(3)$  Å,  $b = 11.498(7)$  Å, and  $c = 12.349(9)$  Å and  $\beta = 106.61(5)^\circ$ . While compound **1** is one-dimensional, with the manganese(II) ions bridged by double  $\mu_{1,5}$ -dicyanamide ligands, the structural arrangement in compounds **2** and **3** is three-dimensional based on ladder-like moieties. These units, whose steps are bipym groups, extend through  $\mu_{1,5}$ -dca bridges and are connected to another four on the plane perpendicular to the extension of the ladders to form the 3D arrangement. Magnetic susceptibility measurements show antiferromagnetic couplings in all cases, increasing for **1**, **3**, and **2**, respectively.

## Introduction

Considerable ongoing research has been directed, over the last years, at the design and preparation of coordination metal complexes with multidimensional network structures. Thus, the preparation of crystalline materials exhibiting some desired structural and topological features becomes a fascinating challenge as it implies the control on the related physical and chemical properties. In this sense, the strategy of synthesis has been widely confirmed to be a determinant factor.

Among the variety of extended frameworks reported during the last years, there are plenty of examples that could illustrate the relevance of the synthesis strategy. Since the azide pseudohalide has been one of the most used ligands,<sup>1</sup> a trio of our azide systems can be mentioned in this context. For instance, the compound  $[\text{Mn}(\text{N}_3)_2\text{terpy}]_2$  (terpy = tridentate 2,2',2''-terpyridine) consists of a dinuclear structure with double end-on azido bridges.<sup>2</sup> The substitution of the tridentate terpyridine by the bidentate 2,2'-bipyridine (bipy) ligand led to the 1D compound  $[\text{Mn}(\text{N}_3)_2\text{bipy}]_n$ , where the Mn(II) ions are alternatively bridged by double end-on (EO) and double end-to-end (EE) azide bridges.<sup>3</sup> Furthermore, the substitution of bipy by the tetradentate bipym (2,2'-bipyrimidine) in a M:bipym molar ratio of 2:1 provokes the connection of the Mn chains resulting in the 2D compound  $[\text{Mn}_2(\text{N}_3)_4\text{bipym}]_n$ . It shows a 2D honeycomblike

structure where the sheets consists of an infinite hexagonal array of Mn(II) ions bridged by bis-chelating bipym and double EO azide bridges.<sup>4</sup> The bipym ligand easily forms  $[\text{M}-\text{bipym}-\text{M}]^{4+}$  dinuclear units<sup>5</sup> that can be used as starting products for higher dimensional materials.

In this context, a further step on the synthesis strategy could consist of the substitution of the azide group by other mononegative bridging ligand, to generate new  $(\text{M}-\text{bipym}-\text{L}_2)$  compounds ( $\text{L} = \text{bridging ligand}$ ). With this aim in mind, we have selected dicyanamide (dca), a ligand that, similarly to azide, exhibits a great versatility in its coordination modes. Thus, besides the monodentate terminal coordination,<sup>6</sup> bidentate,<sup>7</sup> tridentate,<sup>8</sup> and even tetradentate<sup>9</sup> fashions have been reported for dca (Chart 1). The potentiality of dca for the preparation of extended frameworks is illustrated by the great deal of attention ultimately focused on coordination polymers containing this ligand.<sup>10</sup>

Taking into account the above-mentioned aspects, three compounds of general formula  $[\text{M}_n(\text{dca})_{2n}\text{bipym}]$  ( $M$  is a divalent cation) have been synthesized and magnetostructurally

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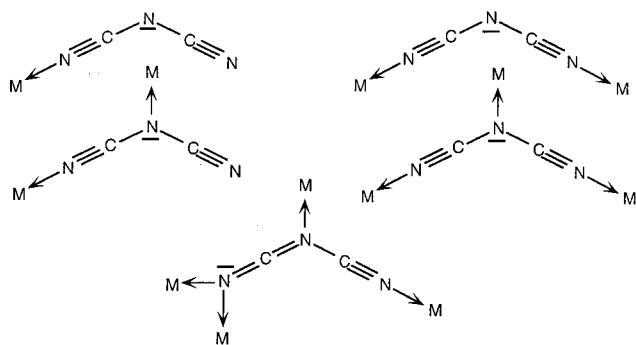
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Chart 1



characterized. Compound **1** ( $M = \text{Mn}$ ,  $n = 1$ ) consists of alternating chains and is isomorphous with  $[\text{Mn}(\text{dca})_2\text{bipy}]$ .<sup>11</sup> For the **2** and **3** compounds a ladderlike moiety can be proposed as a basic structural unit whose repetition leads to a 3D network.

### Experimental Section

**Materials.** Copper(II) nitrate trihydrate, manganese(II) nitrate hexahydrate (Aldrich), 2,2'-bipyrimidine (Lancaster), and sodium dicyanamide (Aldrich) were purchased and used without further purification.

**Synthesis. (a)  $[\text{Mn}(\text{dca})_2\text{bipym}]$  (**1**).** **1** was synthesized by slow addition of a methanolic solution (15 cm<sup>3</sup>) containing sodium dicyanamide (0.178 g, 2 mmol) and  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.287 g, 1 mmol) to a solution of 2,2'-bipyrimidine ligand (0.158 g, 1 mmol) in the same solvent (5 cm<sup>3</sup>). Yellow prismatic crystals appeared after 1–2 weeks from the resulting solution, which was left standing at room temperature. The crystals were filtered out, washed with ether, and dried in air. Yield: 71%. Anal. Found (calcd for  $\text{C}_{12}\text{H}_6\text{N}_{10}\text{Mn}$ ): Mn, 15.7 (15.9); N, 40.5 (40.6); C, 41.9 (41.8); H, 1.7 (1.7).

**(b)  $[\text{M}_2(\text{dca})_4\text{bipym}]$  ( $M = \text{Cu}, \text{Mn}$ ) (**2**, **3**).** These were obtained by adding solid bipym ligand (0.079 g, 0.5 mmol) to a methanolic solution (15 cm<sup>3</sup>) containing  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.242 g, 1 mmol) or  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.287 g, 1 mmol) for **2** and **3**, respectively, followed by the ulterior addition of dicyanamide ligand (0.178 g, 2 mmol). The reaction was carried out under continuous stirring at room temperature. Yellow prismatic crystals appeared in both cases after 1–2 weeks from the resulting solution, which was left standing at room temperature. The crystals were filtered out, washed with ether, and dried in air. Analytical data for **2** are as follows. Yield: 80%. Found (calcd for  $\text{C}_{16}\text{H}_6\text{N}_{16}\text{Cu}_2$ ): Cu, 23.3 (23.1); C, 35.3 (35.0); N, 40.3 (40.8); H, 1.1 (1.1). Analytical data for **3** are as follows. Yield: 68%. Found (calcd for  $\text{C}_{16}\text{H}_6\text{N}_{16}\text{Mn}_2$ ): Mn, 20.4 (20.6); C, 36.1 (36.1); N, 42.0 (42.1); H, 1.1 (1.1).

**Physical Techniques.** Microanalyses were performed with a LECO CHNS-932 analyzer. Analytical measurements were carried out in an ARL 3410 + ICP with Minitorch equipment. IR spectroscopy was

**Table 1.** Crystal Data and Structure Refinement for Compounds **2** and **3**

compound	<b>2</b>	<b>3</b>
chem formula	$\text{C}_{16}\text{H}_6\text{N}_{16}\text{Cu}_2$	$\text{C}_{16}\text{H}_6\text{N}_{16}\text{Mn}_2$
fw	549.45	532.25
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
$a$ , Å	7.540(3)	7.396(3)
$b$ , Å	11.440(7)	11.498(7)
$c$ , Å	11.757(8)	12.349(9)
$\beta$ , deg	106.66(5)	106.61(5)
$V$ , Å <sup>3</sup>	971.6(1)	1006.3(1)
$Z$	2	2
$T$ , °C	25	25
$\lambda$ , Å	0.710 69	0.710 69
$\rho_{\text{obsd}}$ , g cm <sup>-3</sup>	1.89(4)	1.74(3)
$\rho_{\text{calcd}}$ , g cm <sup>-3</sup>	1.878	1.757
$\mu$ , mm <sup>-1</sup>	2.24	1.30
$R(F_o)^a$	0.031	0.035
$R_w(F_o^2)^b$	0.078	0.095

$$^a R(F_o) = [\Sigma|\Delta F|/\Sigma|F_o|]. \quad ^b R_w(F_o^2) = [\Sigma\{w(\Delta F^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}.$$

performed on a Nicolet 520 FTIR spectrophotometer in the 400–4000 cm<sup>-1</sup> region. Magnetic susceptibility and magnetization measurements were carried out on powdered samples in gelatin capsules in the temperature range 4–300 K using a Quantum Design Squid magnetometer, equipped with a helium continuous-flow cryostat. Samples were cooled in zero field, and the data were collected in a 1000 G field upon warming. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms from Pascal's constants.

**X-ray Structural Determinations.** Diffraction data for **2** and **3** were collected at room temperature on a Enraf-Nonius CAD4 four-circle automated diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.710 69$  Å). Details on crystal data, intensity collection and some features of the structure refinement for the two compounds are reported in Table 1. Lattice parameters were determined from automatic centering of 25 reflections ( $12^\circ < \theta < 21^\circ$ ) and refined by least-squares method. The intensities of three standard reflections were measured every 2 h and showed no significant decrease in intensity.

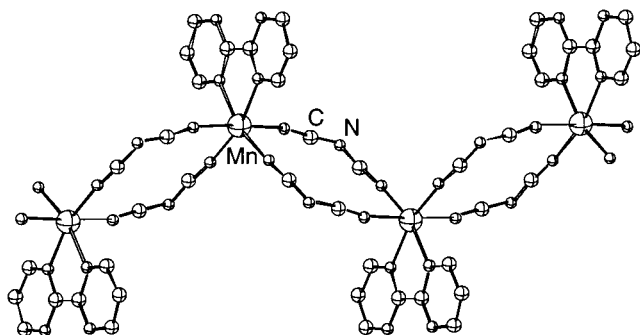
For compound **2**, 2962 reflections were measured in the range  $5 \leq 2\theta \leq 60^\circ$ . A total of 2828 reflections are assumed as observed fulfilling the criteria  $I \geq 2\sigma(I)$ . For compound **3**, 2802 reflections were measured in the range  $5 \leq 2\theta \leq 60^\circ$ , 2677 of which were nonequivalent by symmetry. A total of 2585 reflections were assumed as observed applying the condition  $I \geq 2\sigma(I)$ . Corrections for Lorentz–polarization and extinction effects were done for both compounds. Both structures were solved by direct methods, using the SHELXS<sup>12</sup> computer program, and refined by full-matrix least-squares methods, using the SHELX93<sup>13</sup> computer program. The scattering factors were taken from ref 14. Anisotropic thermal parameters were assigned to all non-hydrogen atoms in both compounds. A total of 3 H atoms were located from a difference synthesis and refined with an overall isotropic temperature factor. The final R factors were  $R(F_o) = 0.031$  ( $wR(F_o) = 0.078$ ) for compound **2** and  $R(F_o) = 0.035$  ( $wR(F_o^2) = 0.095$ ) for compound **3**. Maximum and minimum peaks in the final difference synthesis were 0.398,  $-0.406$  and  $0.564$ ,  $-0.563$  e Å<sup>-3</sup> for compounds **2** and **3**, respectively.

### Results and Discussion

**Synthesis.** The difference in the synthetic method has been a determinant factor for obtaining either **1** or **3** (and **2**). In the former, the metal salt was added to the bipym ligand in a 1/1 proportion leading to compound **1**, while, for the other two, the bipym ligand was added to the metal salts and the proportion ligand/metal was 1/2.

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**Figure 1.** Schematic representation of the 1D structure of compound 1.

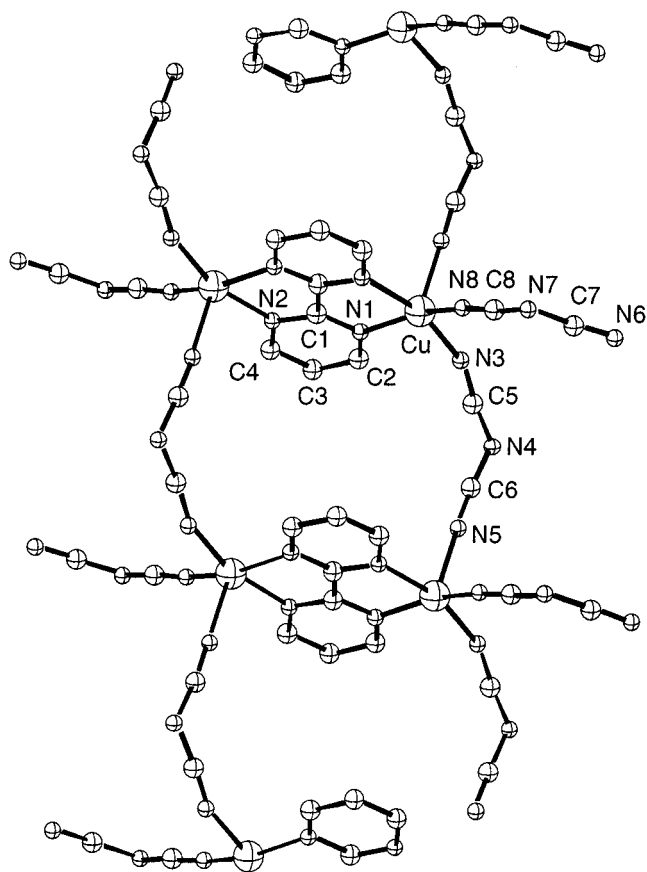
**Infrared Spectra.** The most important aspects concerning the infrared spectra of compounds 1–3 deal with the possibility of characterizing the presence of the different coordination modes of the bipym and dicyanamide ligands.

The three compounds exhibit strong absorptions at 2155, 2225, 2245, 2295, and 2325  $\text{cm}^{-1}$  that correspond to  $\nu_{\text{C}\equiv\text{N}}$  modes of dicyanamide. For compound 1, the quasi-symmetric doublet characteristic of chelating bipym is observed at 1573, 1553  $\text{cm}^{-1}$  (strong). For compounds 2 and 3, strong bands at about 1580  $\text{cm}^{-1}$  (with a shoulder at lower wavenumbers) have been attributed<sup>15</sup> to the asymmetric doublet characteristic of ring stretching for bis-chelating bipym.

**Description of the Structures.** (a) [Mn(dca)<sub>2</sub>bipym] (1). Compound 1 is isomorphous with [Mn(dca)<sub>2</sub>bipy]<sub>n</sub>,<sup>11</sup> having similar lattice parameters and showing equivalent powder diffraction patterns. Thus, it consists of 1-D zigzag chains (Figure 1). These chains are formed by double  $\mu_{1,5}$ -dicyanamide bridges, which, due to the bidentate coordination of the bipym ligand, leads to a cis disposition of the bridging dicyanamides. Four coordination sites are occupied by N<sub>dca</sub> atoms, while the two remaining positions are occupied by two N<sub>bipym</sub> atoms of the bipyrimidine ligand which acts as a terminal one.

(b) [M<sub>2</sub>(dca)<sub>4</sub>bipym] (M = Cu, Mn) (2, 3). Compounds 2 and 3 consists of 3D networks, where, as observed in Figures 2 and 3, each Cu(II) and Mn(II) cations are octahedrally bonded to one bipym (through N1 and N2 atoms) and four dca ligands (two N3–C5–N4–C6–N5 groups and two N6–C7–N7–C8–N8 groups). The two N<sub>bipym</sub> atoms occupy two of the equatorial positions. Since the bipym's perform as tetradentate ligands, they allow the connection between two metallic cations. On the other hand, the four dca groups act as  $\mu_{1,5}$ -bridges with the N3 and the N8 atoms on the remaining equatorial positions and N5 and N6 on the axial ones. As a result, each of the Cu(II) or Mn(II) cations are linked to five metallic centers: one through bipym (Cu $\cdots$ Cu distance is 5.544 Å; Mn $\cdots$ Mn distance is 6.156 Å) and four by dca ligands (Cu $\cdots$ Cu distances through (N3-, N5-) and (N6, N8)-bonded dca groups are 7.396 and 7.656 Å, respectively).

The 3D structures for 2 and 3 can also be described on the basis of covalently interconnected ladderlike moieties (Figure 4) whose steps are the bipym groups. The direction of the extension of these units is [100], with the N3–C5–N4–C6–N5 dca groups being the responsible ligands for the propagation. Each ladder unit is connected to another four along the [011] and [0 $\bar{1}$ 1] directions of the (011) planes. These links take place through N6–C7–N7–C8–N8 dca groups.



**Figure 2.** ORTEP view (50% probability) of the structure for 2.

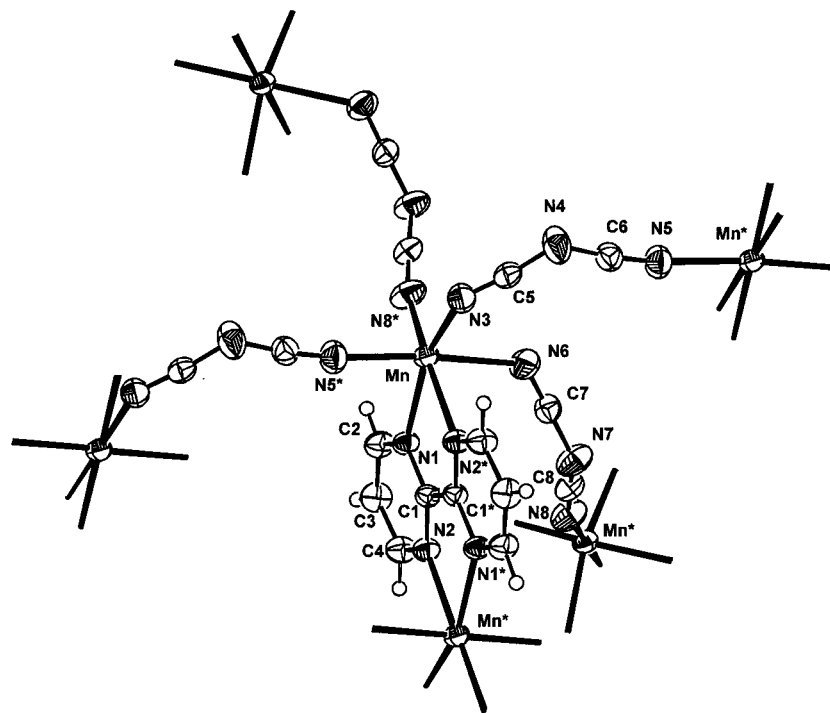
Table 2 summarizes the selected bond distances and angles for 2 and 3. The M–N distances are similar, the M–N<sub>bipym</sub> values being higher than the M–N<sub>dca</sub> ones. As expected, the coordination polyhedron corresponding to the Mn(II) compound is more regular than that corresponding to the copper(II) one, which shows an elongated octahedron in agreement with the plasticity of this ion. In this case, the long Cu–N6 distance must be noticed. Thus, the corresponding value of 3.25 Å clearly implies that the covalent connection between distinct ladderlike units is weak. In relation to the bond angles, it must be noticed that the rigid bipym imposes an important distortion on the coordination sphere that is illustrated by the fact that the values involving N<sub>bipym</sub> atoms (N1 and N2) are far from the ideal ones (N1–M–N2 bipym bite angles are close to 70 and 80°, which leads to the other equatorial angles being slightly larger than 90°). As expected, the bipym bite angles, 70.84(6)° (Mn), and 79.39(17)° (Cu), are inversely related to the ionic radii of the metal centers.

The dicyanamide ligands are bent, with C5–N4–C6 and C7–N7–C8 angles around 120° and two N–C–N straight linear units with angles near 175° in both cases.

**Magnetic Data and Coupling Constant Evaluation.** The magnetic characterization of compounds 1–3 was carried out through measurements of the variation of the magnetic susceptibility,  $\chi_m$ , with temperature. The experimental data, plotted as the thermal variation of the susceptibility  $\chi_m$  and the product  $\chi_m T$  are shown in Figure 5 for compounds 1 and 3 and in Figure 6 for compound 2. The overall behavior of 1 and 3 corresponds to weak and moderate antiferromagnetically coupled systems, respectively. While for compound 2, strong antiferromagnetism is observed.

The thermal variation of the molar magnetic susceptibility  $\chi_m$  for compound 1 shows that  $\chi_m$  values continuously increase

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**Figure 3.** ORTEP view (50% probability) of the structure for **3**.

on cooling. When the samples are cooled, the  $\chi_m T$  vs  $T$  data decrease slowly from 300 K, more quickly below 50 K, and tend to zero down to 4 K. The value of  $\chi_m T$  at room temperature is  $4.3 \text{ cm}^3 \text{ K mol}^{-1}$  ( $\mu_{\text{eff}} = 5.86 \mu_B$ ), which is slightly lower than the  $4.52 \text{ cm}^3 \text{ K mol}^{-1}$  ( $\mu_{\text{eff}} = 5.92 \mu_B$ ) expected for isolated  $S = 5/2$  ions. It is in agreement with slight antiferromagnetic interactions in the compound.

The magnetic behavior of compound **1** has been analyzed by means of the analytical expression<sup>16</sup> for an infinite chain of classical spins, scaled to  $S = 5/2$ , derived by Fisher (eq 1):

$$\chi = \left[ \frac{Ng^2\beta^2S(S+1)}{3kT} \right] \left[ \frac{1+u}{1-u} \right]$$

Here  $N$  is Avogadro's number,  $k$  is the Boltzmann constant,

$$u = \coth \left[ \frac{JS(S+1)}{kT} - \frac{kT}{JS(S+1)} \right] \quad (1)$$

and  $\beta$  is the Bohr magneton.

The best fit leads to  $J = -0.18 \text{ cm}^{-1}$  (0.27 K),  $g = 2.00$ , which is slightly lower than the  $J$  value obtained for the related bipym compound.<sup>11</sup> The agreement factor (defined as  $SE = [\Phi/(n - K)]^{1/2}$ , where  $n$  is the number of data points,  $K$  is the number of adjustable parameters (1), and  $\Phi = \sum [\chi_m T_{\text{obs}} - \chi_m T_{\text{calc}}]^2$  is the sum of squares of the residuals) using the above expression was  $6.3 \times 10^{-4}$ , which actually corresponds to an excellent experiment–theory agreement. Considering the structural features, the observed  $J = -0.18 \text{ cm}^{-1}$  value can be explained on the basis of the possible exchange pathways present in this compound. Thus, the  $\mu_{1,5}$ -dicyanamide bridges provide weak coupling in the few examples of compounds measured to date.<sup>11a</sup>

The  $\chi_m$  values for **3** (Figure 5) increase from  $1.34 \times 10^{-2} \text{ cm}^3 \text{ mol}^{-1}$  at room temperature, up to a maximum ( $1.87 \times 10^{-1} \text{ cm}^3 \text{ mol}^{-1}$  at 7 K), and afterward decrease tending to zero. The Curie–Weiss law is followed down to 50 K with values of  $C_m$

and  $g$  of  $4.24 \text{ cm}^3 \text{ K mol}^{-1}$  and 1.97, respectively (typical for octahedral Mn(II)). The Weiss temperature has been observed to be  $\Theta = -12.0 \text{ K}$ . On the other hand, the  $\chi_m T$  curve continuously decreases upon cooling from  $4.04 \text{ cm}^3 \text{ K mol}^{-1}$  ( $\mu_{\text{eff}} = 5.68 \mu_B/\text{Mn atom}$ ) at RT tending to zero (Figure 5). This value is also lower than the one expected for isolated  $S = 5/2$  ions ( $4.52 \text{ cm}^3 \text{ K mol}^{-1}$ ;  $\mu_{\text{eff}} = 5.92 \mu_B$ ) being indicative of moderate antiferromagnetic interactions.

To evaluate the antiferromagnetic interactions responsible for the magnetic behavior of **3**, it may be considered that since the  $\mu_{1,5}$ -dca ligand behaves as a poor magnetic mediator ( $-J/k_B = 0.10\text{--}0.18 \text{ K}$ ),<sup>11a</sup> these interactions should be mainly attributed to the exchange through the bipym ligand, which is a much better mediator ( $-J/k_B = 0.9\text{--}14 \text{ K}$ ).<sup>17</sup> In that case, a dinuclear model ( $S_{\text{tot}} = 5/2 \pm 5/2$ ) could account for the magnetic behavior of **3**. Thus, the magnetic susceptibility data can be analyzed in terms of the dipolar coupling approach for a Mn(II) dimer. The expression for the magnetic susceptibility (eq 2), based on the isotropic spin Hamiltonian  $\hat{H} = -J\hat{S}_A \cdot \hat{S}_B$  ( $S_A = S_B = 5/2$ ) and derived from Van Vleck's equation, is

$$\chi_m = \frac{N\beta^2 g^2}{kT} \left[ \frac{55 + 30 \exp(10X) + 14 \exp(18X) + 5 \exp(24X) + \exp(28X)}{11 + 9 \exp(10X) + 7 \exp(18X) + 5 \exp(24X) + 3 \exp(28X) + \exp(30X)} \right] \quad (2)$$

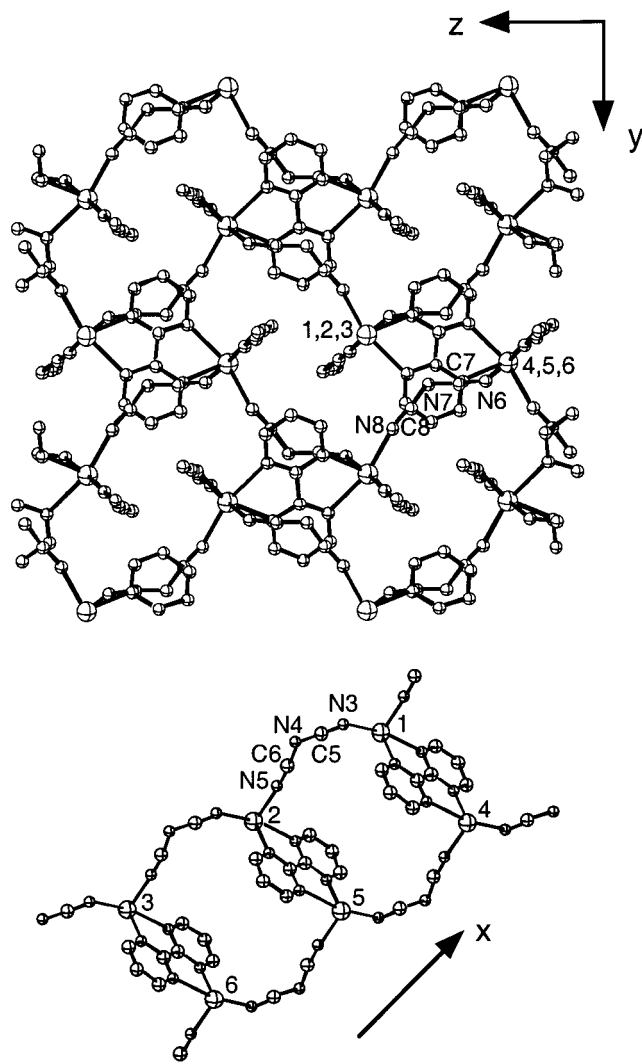
As observed in Figure 5, this model quite accurately

$$X = -J/kT$$

reproduces the experimental data with values of  $J$  and  $g$  of  $-0.86 \text{ cm}^{-1}$  (1.24 K) and 1.97, respectively (agreement factor:  $6.3 \times 10^{-4}$ ). The sign and magnitude of the exchange constant  $J$  calculated for the interaction through bipym are comparable to others found in the literature. Thus, values around  $-1 \text{ cm}^{-1}$

(16) Fisher, M. E. *Am. J. Phys.* **1964**, *32*, 343.

(17) De Munno, G.; Viau, G.; Julve, M.; Lloret, F.; Faus, J. *Inorg. Chim. Acta* **1997**, *257*, 121.



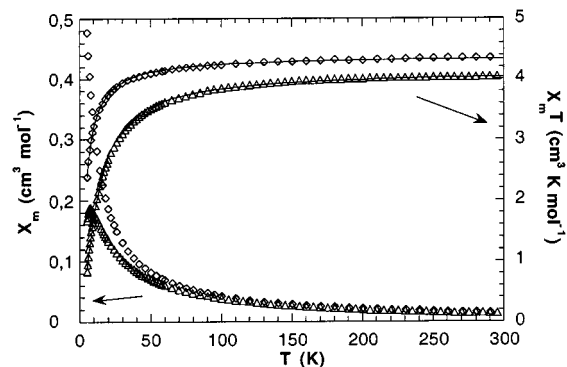
**Figure 4.** View of the 3D structure for **2** and **3** on the *yz* plane (top) and detail along the *x* direction showing the ladderlike moieties (bottom).

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for Compounds **2** and **3**<sup>a</sup>

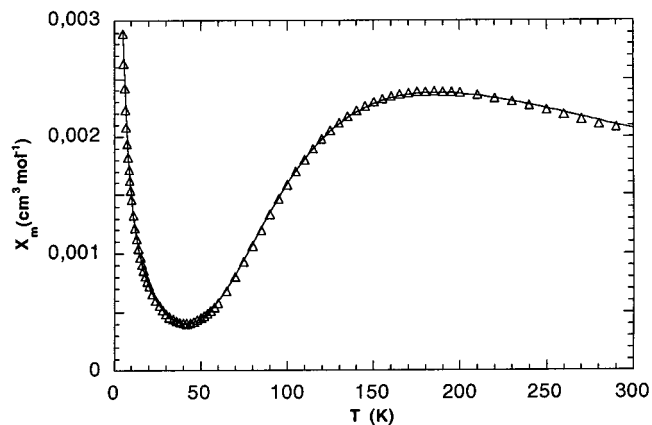
Compound <b>2</b>			
Cu–N(1)	2.052(2)	N(3)–Cu–N(5b)	100.7(2)
Cu–N(2a)	2.085(4)	N(3)–Cu–N(6)	99.1(2)
Cu–N(3)	2.153(5)	N(5b)–Cu–N(6)	95.1(2)
Cu–N(5b)	1.943(5)	N(5b)–Cu–N(1)	163.3(2)
Cu–N(6)	1.952(5)	N(5b)–Cu–N(2a)	89.2(2)
Cu–N(8c)	3.246(2)	N(6)–Cu–N(1)	91.8(2)
Cu···Cu(b)	5.544(2)	N(1)–Cu–N(2a)	79.4(2)
Compound <b>3</b>			
Mn–N(1)	2.298(2)	N(3)–Mn–N(5b)	95.27(8)
Mn–N(2d)	2.360(2)	N(2d)–Mn–N(3)	88.24(8)
Mn–N(3)	2.173(2)	N(3)–Mn–N(8e)	104.92(9)
Mn–N(5b)	2.160(2)	N(5b)–Mn–N(6)	174.93(7)
Mn–N(6)	2.316(2)	N(5b)–Mn–N(8e)	95.12(8)
Mn–N(8e)	2.153(2)	N(6)–Mn–N(8e)	87.03(8)
Mn···Mn(d)	6.156(1)	N(1)–Mn–N(2d)	70.84(6)

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: a =  $-x, 1 - y, -z$ ; b =  $x + 1, y, z$ ; c =  $x - 1, y, z$ ; d =  $-x, 2 - y, 1 - z$ ; e =  $x + 1/2, -y + 3/2, z + 1/2$ .

have been reported for Mn–bipym–Mn dinuclear species.<sup>18</sup> The moderate efficiency of bis-chelating bipym as a magnetic



**Figure 5.** Thermal variation of  $\chi_m$  and  $\chi_m T$  for **1** ( $\diamond$ ) and **3** ( $\Delta$ ). The continuous lines represent the fit to the theoretical models.



**Figure 6.** Thermal variation of  $\chi_m$  for **2**. The continuous line represents the calculated curve for the theoretical model.

coupler is explained by the overlap between  $d_{x^2-y^2}$  magnetic orbitals (*x* and *y* axes being the ones corresponding to the Mn–N<sub>bipym</sub> bonds) through the symmetry-adapted HOMO of the bipym bridge.<sup>19</sup> The fact that the Mn–bipym–Mn fragment is practically planar favors the overlapping, increasing the magnitude of the exchange coupling.

Finally, the thermal variation of the magnetic susceptibility for the copper compound **2** let us to observe strong antiferromagnetic interactions (Figure 6). A smooth maximum appears in the thermal variation of the susceptibility at about 150 K, and the curve increases at low temperature due to the occurrence of uncoupled species. The  $\chi_m T$  value decreases rapidly from room temperature (the  $\chi_m T$  value, per Cu atom, at 300 K is  $0.3 \text{ cm}^3 \text{ K mol}^{-1}$  ( $\mu_{\text{eff}} = 1.55 \mu_B$ ), a smaller value than that expected for an uncoupled Cu<sup>II</sup> ion), showing a plateau in the interval 50–0 K. This behavior should clearly be associated to the great ability of the bipym bridges to transmit antiferromagnetic interactions in a planar Cu–bipym–Cu unit.

The magnetic behavior of this compound must then be explained assuming a dinuclear model for two  $S = 1/2$  ions, by using the Bleaney–Bowers equation,<sup>20</sup> modified to include an amount of  $\rho\%$  uncoupled species

$$\chi = \frac{2Ng^2\beta^2(1 - \rho)}{kT(3 + \exp(-J/kT))} + \rho C/T \quad (3)$$

where *J* expresses the singlet–triplet energy gap and *N*, *g*,  $\beta$ ,

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(18) De Munno, G.; Ruiz, R.; Lloret, F.; Faus, J.; Sessoli, R.; Julve, M. *Inorg. Chem.* **1995**, *34*, 408.

and  $k$  have their usual meaning. In this case, the best fit result gives  $J$ ,  $g$ , and  $\rho$  values of  $-76 \text{ cm}^{-1}$  ( $-109.64 \text{ K}$ ), 2.17, and 1.2%, respectively (agreement factor:  $2.1 \times 10^{-3}$ ). These values are also in good agreement with those obtained for dinuclear Cu–bipym–Cu entities in the literature.<sup>21</sup> Thus, these units are planar and the magnetic orbitals of the Cu(II) ions, namely  $d_x^2-y^2$ , can strongly interact through bipyrimidine ligand.

### Concluding Remarks

The combined use of dca and bipym has led to the preparation of three extended frameworks with Mn(II) and Cu(II). Even if these compounds have been synthesized under similar conditions, two types of structural array have been obtained depending on the synthesis way: 1D for  $[\text{Mn}(\text{dca})_2(\text{bipym})]$  (**1**), where the metal salt was added on the bipym ligand in 1/1 proportion; 3D for  $[\text{M}_2(\text{dca})_4(\text{bipym})]$  ( $\text{M} = \text{Cu}$  (**2**),  $\text{Mn}$  (**3**)), where the bipym ligand was added on the metals in 1/2 proportion. The former exhibits a zigzag chain structure with double dicyana-

mide bridges, while **2** and **3** exhibit as basic structural unit a ladderlike moiety, whose steps are the bipym ligands, which extend through single  $\mu_{1,5}$ -dca bridges to form the three-dimensional architecture. The weak antiferromagnetic interactions for **1** are in agreement with the existence of double  $\mu_{1,5}$ -dicyanamide bridges, while for compounds **2** and **3** strong and moderate antiferromagnetic interactions are associated to the bipyrimidine bridges.

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**Supporting Information Available:** Two X-ray crystallographic files (**2** and **3**) in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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